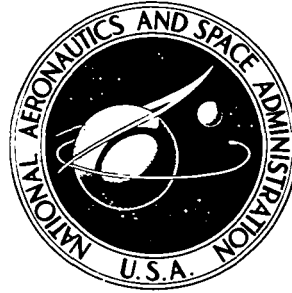


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**PREPARATION AND EVALUATION OF  
THIN-FILM SODIUM TUNGSTEN BRONZES**

*by Harold E. Kautz, William L. Fielder, Joseph Singer,  
and J. Stuart Fordyce*

*Lewis Research Center  
Cleveland, Ohio 44135*

1. Report No. NASA TM X-2985		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle  PREPARATION AND EVALUATION OF THIN-FILM SODIUM TUNGSTEN BRONZES				5. Report Date January 1974	
				6. Performing Organization Code	
7. Author(s) Harold E. Kautz, William L. Fielder, Joseph Singer, and J. Stuart Fordyce				8. Performing Organization Report No. E-7668	
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135				10. Work Unit No. 502-05	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546				13. Type of Report and Period Covered Technical Memorandum	
				14. Sponsoring Agency Code	
15. Supplementary Notes					
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17. Key Words (Suggested by Author(s)) Thin films Ionic Conductivity Reversible Electrodes Electrochemistry			18. Distribution Statement Unclassified - unlimited  Cat. 18		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified		21. No. of Pages 12	22. Price* \$2.75	

# PREPARATION AND EVALUATION OF THIN-FILM SODIUM TUNGSTEN BRONZES

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## SUMMARY

Thin films of sodium tungsten bronze ( $\text{Na}_x\text{WO}_3$ ) were investigated as reversible sodium ion electrodes for solid electrolytes. The films were made by electron beam evaporation of the three phases, W metal,  $\text{Na}_2\text{WO}_4$ , and  $\text{WO}_3$ , followed by sintering. The substrates were sodium beta alumina disks and glass slides. X-ray analyses of the films showed that sintering in dry nitrogen with prior exposure to air lead to a mixture of phases, including  $\text{Na}_2\text{W}_4\text{O}_{13}$  and a bronze phase. Sintering in vacuum with no air exposure produced tetragonal I bronze with a nominal composition of  $\text{Na}_{0.31}\text{WO}_3$ , single phase within the limits of x-ray diffraction detectability.

The films were uniform and adherent on sodium beta alumina substrates. The ac and dc conductivities were measured for the beta alumina with the sodium tungsten bronze films as electrodes. These experiments indicated that the tetragonal I bronze electrodes were not completely reversible. This may have resulted from sodium ion blocking within the film or at the bronze beta alumina interface. The irreversibility may be due to excess unreacted starting material.

## INTRODUCTION

Solid alkali ion conductors with high conductivity are of interest as solid electrolytes in high energy density battery systems. The present work is part of a search for and an evaluation of potential solid electrolytes, and it includes the development and refinement of evaluation techniques (refs. 1 to 3). For an accurate determination of the conductivities of conductors having high ion diffusivity, reversible electrodes should be used.

Polycrystalline, tetragonal I sodium tungsten bronze ( $\text{Na}_{0.4}\text{WO}_3$ ) has been used for electrodes to measure the conductivities of single-crystal sodium beta alumina (ref. 4). It was found that polarization was minimal when measurements were made at 10 000 hertz even at temperatures as low as  $-150^\circ\text{C}$ .

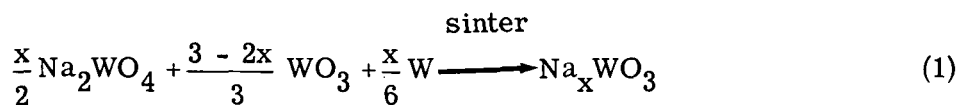
Tungsten bronzes, in general, may therefore be of interest as reversible electrodes for solid alkali ion conductors. They have the formula  $\text{M}_x\text{WO}_3$  where M is the alkali metal ion and x varies between 0 and 1. This series of compounds exhibits both electronic and M-ion conductivity (ref. 4). Apparently both conductivities increase with x within a given phase.

Vapor-deposited thin films of these alkali tungsten bronzes may present unique advantages as electrodes. First, vacuum coating the solid electrolyte sample with an electrode material may permit the formation of less contaminated interfaces than might be expected from a bulk to bulk bonding procedure. Second, vacuum deposition allows a wide range of electrode configurations and is applicable to the fabrication of contacts on many samples in one deposition run.

Our initial choice of sodium as the alkali ion in  $\text{M}_x\text{WO}_3$  was dictated by the immediate applicability to the solid electrolyte sodium beta alumina  $\text{Na}_20.9\text{Al}_2\text{O}_3$  (ref. 5). This report describes the preparation of thin-film electrodes of tetragonal I sodium tungsten bronze on polycrystalline sodium beta alumina and on glass, the study of the reversibility of the electrodes by ac and dc conductivity measurements, and a comparison of the results with those reported by Whittingham (ref. 4).

## EXPERIMENTAL

The chemical reaction for synthesis of sodium tungsten bronze is given by (ref. 6)



In the present work, prior to sintering, each starting material was evaporated separately in the following order: tungsten metal, sodium tungstate, and then tungsten trioxide. The assumption was made that these materials vaporize congruently (ref. 7). This method was chosen after considering radiofrequency sputtering and electron beam evaporation of  $\text{Na}_x\text{WO}_3$  directly. The sequential method does not require preliminary fabrication of the desired compound and lends itself most easily to the variation of the x value from run to run.

Starting materials were reagent grade powders of these chemicals pressed into 1.27-centimeters - (0.5 in.) diameter pellets weighing about 3 grams each. A commercial multihearth electron beam gun was used for these evaporations. The apparatus is shown schematically in figure 1. The hearths are mounted on a turntable which allows successive remote rotation of each hearth into the electron beam while maintaining a vacuum in the chamber. This equipment allows deposition of films of the three starting materials without intermediate exposure to air. The substrates in the case of glass were standard 2.54 by 7.62 centimeter (1 by 3 in.) slides. The sodium beta alumina sample was a disk with a 1.27-centimeter (0.5-in.) diameter. They were suspended in a holder facing downward 36 centimeters (14 in.) above the electron beam hearth. The accelerating voltage for the electron beam was 10 000 volts. Evaporations were started when the chamber pressure was below  $10^{-5}$  torr. During the evaporation the chamber pressure remained below  $10^{-4}$  torr. The weight of each deposited starting material per unit area was determined with a quartz crystal monitor to no worse than  $\pm 6$  percent. Each reactant was deposited until the desired nominal  $x$  value (according to eq. (1)) was obtained.

For tungsten evaporations, an electron beam current of about 200 milliamperes was employed. With this current a small melt was formed on the top of the pressed powder pellets. Deposition rates of about  $1 \times 10^{-8}$  to  $5 \times 10^{-8}$  gram per square centimeter per second were obtained. The tungsten source could be used repeatedly. In the case of the sodium tungstate, the beam current varied between 20 and 50 milliamperes. This was sufficient to melt the pellet completely. When fresh material for each run was introduced, a preheating step was employed to drive off the water of hydration. Even then, the melt was susceptible to "bumping." Deposition rates varied from  $6 \times 10^{-8}$  to  $4 \times 10^{-7}$  grams per square centimeter per second. Tungsten trioxide was evaporated at a beam current of less than 10 milliamperes. This material sublimes rather than melts, so it was necessary to scan the beam around the hearth in both axes to evaporate sufficient material. After evaporation the residue was yellow-blue in color, probably indicative of reduction. Fresh tungsten trioxide was provided for each evaporation. The evaporation rate for this material varied from  $2 \times 10^{-7}$  to  $10 \times 10^{-7}$  gram per square centimeter per second.

In the earlier experiments the  $x$  value was purposely varied over more than one phase. Glass slides were substrate. After exposure to air, sintering was performed at 1 atmosphere in dry nitrogen. The composition of the sintered films was determined by visual examination of x-ray diffraction powder patterns.

For the later experiments (as illustrated by samples A and B), a polycrystalline sodium beta alumina disk of about 95 percent density was used as the substrate. A film of about 1.5 micrometers of sodium tungsten bronze of nominal formula  $\text{Na}_{0.31}\text{WO}_3$  was deposited on both faces of the disk and on an adjacent glass slide. The film thick-

ness was determined with a moving stylus thickness monitor. The samples were vacuum sintered at 300° to 450° C without intermediate exposure to air. The film phase compositions for samples A and B were determined by an x-ray analysis of the deposits on the glass slides. For sample B, a film deposited on a beta alumina substrate was also analyzed for comparing the composition with the slide from the same run.

Prior to making electrical measurements, sample A ( $\text{Na}_{0.31}\text{WO}_3$ ) was preheated at 100° C in vacuum. After the conductivity measurements the bronze films were removed and new films were deposited on the beta alumina disk. This sample, now called sample B ( $\text{Na}_{0.31}\text{WO}_3$ ), was preheated at a higher temperature, about 500° C, in vacuum in an attempt to improve the bonding of the bronze films to the beta alumina. Helium gas (with less than 5 ppm oxygen or water) was added slowly through a liquid nitrogen trap to a system pressure of about 93 kilonewtons per square meter (700 mm Hg). The system was reevacuated periodically to counteract the slight leakage or degassing.

Because the tungsten bronze films are good electronic conductors, electrical contacts were made easily with platinum foils at about 35 kilonewtons per square meter (5 psi). The ac conductivities of sample B were measured at four frequencies (0.1, 1, 10, and 100 kHz) from 25° to 425° C in helium with an impedance comparator bridge using standard resistors. In addition, the dc conductivities were measured for four temperatures. A constant current of 14 microamperes was passed, and the corresponding voltage across the sample was measured on an oscilloscope for the time interval of 0.1 millisecond to 1 to 10 seconds.

## RESULTS

All films were found to have good adherence to substrates regardless of the sintering method. They could not be wiped off, but they could be scraped off with the edge of a glass slide. On the beta alumina they were more adherent, as one would expect because of roughness, requiring sanding sufficient to take off substrate material. The films appeared quite uniform on the beta alumina. In contrast, pinholes were visible in the films deposited on glass slides.

For films exposed to air prior to sintering in dry nitrogen, x-ray powder patterns revealed the presence of not only  $\text{Na}_x\text{WO}_3$  but also  $\text{Na}_2\text{W}_4\text{O}_{13}$ . The particular bronze phases found were, however, those expected from the  $x$  value calculated from the amounts of starting material (ref. 3).

Film preparation results for samples A and B are shown in table I. It is seen that the vacuum sintering (without prior exposure to air) permitted fabrication of films that were composed of pure phase tetragonal I sodium tungsten bronze. For sample B, where

x-ray analyses were also performed with a film deposited on a beta alumina substrate, the film consisted of pure tetragonal I and was of random orientation.

Nonreproducible conductivity values were obtained for sample A (which was preheated only to 100° C) over the temperature range of 25° to 425° C. Presumably, the bronze films had not adequately bonded to the beta alumina. As a consequence, sample B was preheated to about 500° C. The ac conductivities,  $K$ , of sample B are shown in figure 2 as a function of temperature. The conductivities are dependent on the frequency at the lower temperatures. For example, at 25° C, the conductivities are about  $1.5 \times 10^{-5}$  and  $6.3 \times 10^{-4}$  per ohm per centimeter at 0.1 and 100 kilohertz, respectively. This dependence on frequency decreases at higher temperatures; the conductivity approaches a value of about  $3.1 \times 10^{-3}$  per ohm per centimeter at 400° C. Between 25° and 150° C, the activation energy is 15.5 kilojoule per mole (3.7 kcal/mole) at 10 kilohertz.

For comparison, the conductivities obtained by Whittingham (ref. 4) for single crystal sodium beta alumina, using tetragonal I sodium tungsten bronze electrodes ( $\text{Na}_{0.4}\text{WO}_3$ ), are shown in figure 2 as a dashed line.

The dc conductivities of sample B are shown in figure 3 where the log of the conductivity is plotted against the log of time. A considerable decrease in conductivity occurred with time. For example, at 33° C, the conductivities were about  $6 \times 10^{-5}$  and  $4 \times 10^{-7}$  per ohm per centimeter at 269° C and 1 second.

## DISCUSSION

### Film Fabrication

An exposure to air followed by sintering in dry nitrogen gas caused the formation of a second phase ( $\text{Na}_2\text{W}_4\text{O}_{13}$ ) in the films. As a consequence of this second phase, the  $x$  value in these  $\text{Na}_x\text{WO}_3$  bronzes deviated somewhat from that value calculated from the amounts of the starting materials.

Sintering in vacuum without prior exposure to air, however, lead to single-phase films of sodium tungsten bronze. The relatively low sintering temperatures (below 450° C) may be desirable for applying reversible electrodes in cases where the solid electrolyte may not be stable at higher temperatures.

We have also recently demonstrated that the previous evaporation and vacuum sintering method can be applied to potassium tungsten bronzes. Pure phase films of the hexagonal  $\text{K}_{0.2}\text{WO}_3$  and the tetragonal  $\text{K}_{0.5}\text{WO}_3$  have been obtained with this method. These films are uniform and adherent to potassium beta alumina.

## Electrical Conductivity

The ac conductivities for polycrystalline sodium beta alumina sample B (fig. 2) are compared with the conductivities reported by Whittingham (ref. 4) for a single-crystal sodium beta alumina ( $\text{Na}_{0.4}\text{WO}_3$ ) at 10 kilohertz. The activation energy value of 15.5 kilojoule per mole (3.7 kcal/mole) obtained for sample B at 10 kilohertz over the temperature range of 25° to 150° C is in good agreement with the value of 15.9 kilojoule per mole (3.79 kcal/mole) reported by Whittingham at 10 kilohertz.

As expected, the conductivity values for polycrystalline sample B differ from those obtained by Whittingham for single crystal. For example, at 10 kilohertz the conductivities of sample B were an order of magnitude smaller than those for the single crystal over the temperature range of 25° to 150° C. This difference is largely attributable to the anisotropy of sodium beta alumina which conducts sodium preferentially in the plane perpendicular to the C axis.

From the conductivities, it was inferred that tetragonal I sodium tungsten bronze thin films did not function as perfectly reversible, nonpolarizing electrodes toward sodium ions in the polycrystalline sample B. At the lower temperatures, the ac conductivity decreased with decreasing frequency, and the dc conductivity decreased with increasing time. These effects were less pronounced as the temperature increased.

In a private communication, Whittingham stated that he had also observed these decreases in conductivity with frequency and time. We suggest that these effects at the lower temperatures are due primarily to polarization at the bronze beta alumina interface. At the higher temperature (i. e., 400° C), the conductivities seem to approach a relatively constant value causing the conductivities of sample B to deviate from its linear extrapolated values. We suggest that this apparent limiting conductivity was due primarily to polarization within the bronze thin film.

Although they may not be completely reversible, thin films of evaporated sodium tungsten bronze still may be useful as electrodes for certain sodium ion conductors. For example, they may serve as a useful diagnostic electrode in ac conductivity measurements in the vicinity of 100° to 300° C at the higher frequencies of 10 and 100 kilohertz. Under these conditions, interfacial polarization effects should be less pronounced and electrode polarization effects should be nominal. These bronze electrodes may be particularly useful where reversible liquid electrodes may be difficult or inconvenient for measurements as in the case of highly porous samples where liquid electrodes may lead to internal shorts. Furthermore, for small or irregularly shaped samples where liquid electrodes may be awkward experimentally, evaporated solid bronze films should be relatively easy to apply to most types of samples. Hopefully, improved techniques for attaching and annealing these bronze films to the ionic conducting substrate might make them sufficiently reversible to warrant their use for alkali ion conductors over wider temperature ranges.



Two such techniques for improving electrode reversibility may be considered. First, a slight excess of tungsten metal might be added to ensure a more complete conversion of sodium tungstate and tungsten oxide to tetragonal I sodium tungsten bronze. In a recent experiment, the use of a slight excess of tungsten seemed to produce relatively pure tungsten bronze with no apparent contamination with other phases (e. g.,  $\text{Na}_2\text{W}_4\text{O}_{13}$  or unreacted  $\text{Na}_2\text{WO}_4$  or  $\text{WO}_3$ ). Second, the tungsten metal might be deposited last on tungsten oxide rather than on the sodium beta alumina surface.

During the film preparation, the tungsten metal had been applied first onto the beta alumina sample. If some of this tungsten (particularly that portion adjacent to the beta alumina) had not been completely converted to the tetragonal I sodium tungsten bronze, polarization might have occurred due to a partial blocking of the ions by the metal. Depositing the tungsten last may not only reduce this possibility of ion blocking but may actually improve the electronic contact from the lead wires to the bronze films.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, October 30, 1973,  
502-05.

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TABLE I. - FILMS DEPOSITED ON GLASS SLIDES<sup>a</sup>  
AND SINTERED IN VACUUM

	Sample	
	A	B
Nominal formula	$\text{Na}_{0.31}\text{WO}_3$	$\text{Na}_{0.31}\text{WO}_3$
Sinter time, min	120	120
Sinter temperature, °C	300 to 400	400 to 450
Color	Deep blue	Deep blue
Thickness, $\mu\text{m}$	1.5	1.5
Only phase detected by x-ray diffraction	Tetragonal I bronze	Tetragonal I bronze

<sup>a</sup>Slides were adjacent to sodium beta alumina substrates.

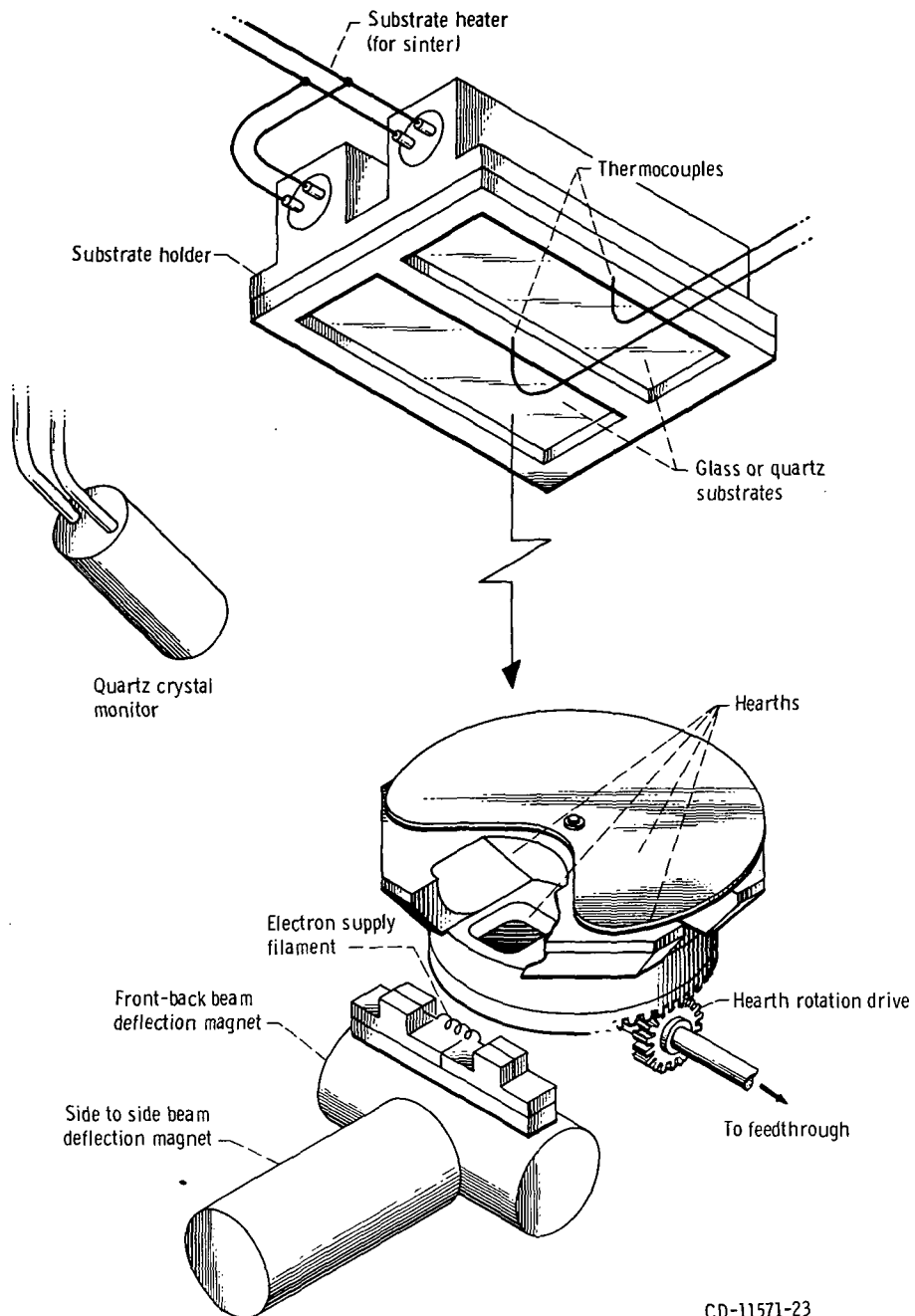


Figure 1. - Electron beam evaporation apparatus.

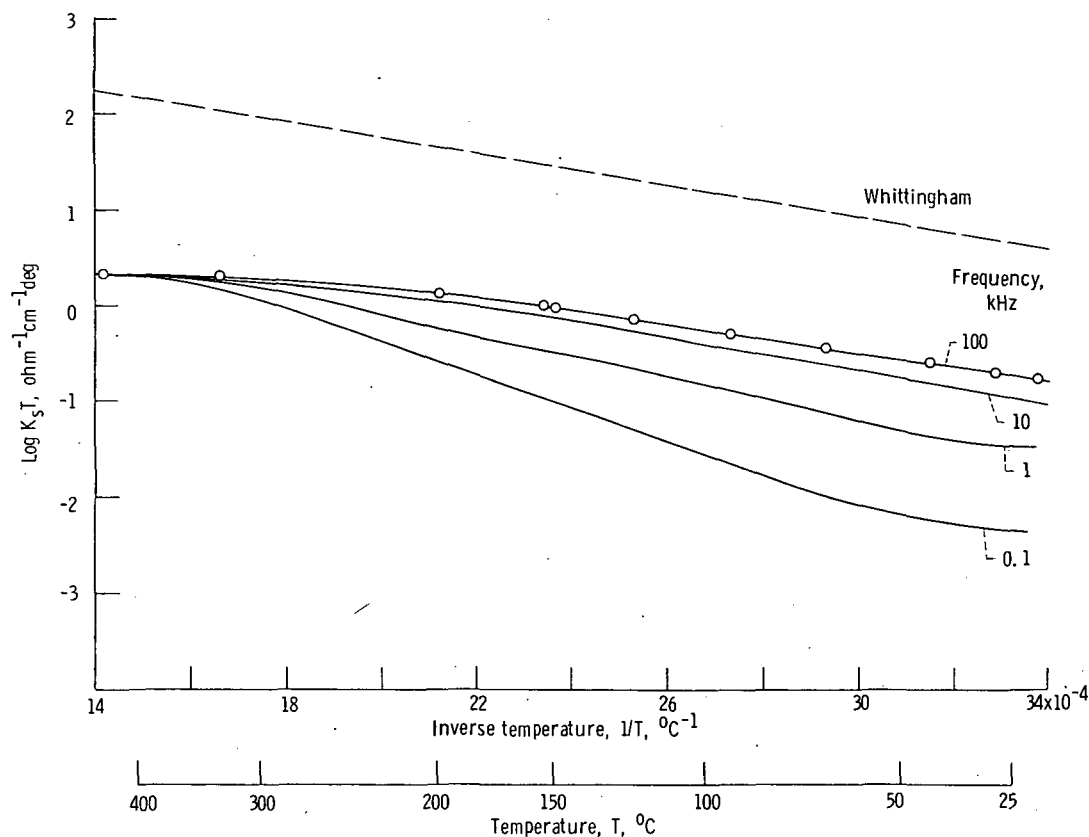


Figure 2. - The ac conductivity of polycrystalline sodium beta alumina (sample B) as function of temperature using sodium tungsten bronze electrodes.

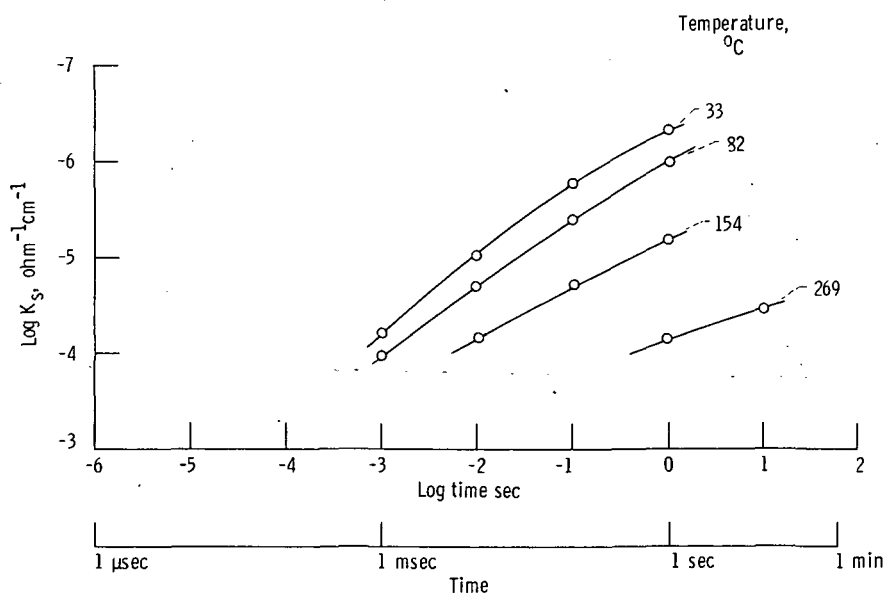


Figure 3. - The dc conductivity of polycrystalline sodium beta alumina (sample B) as function of time using sodium tungsten bronze electrodes.



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